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Liquid fuels, hydrogen and chemicals from lignin: A critical review

Pooya Azadi [a,b,*], Oliver R. Inderwildi [a], Ramin Farnood [b], David A. King [a]

[a] Smith School of Enterprise and the Environment, University of Oxford, 75 George St., OX1 2BQ, Oxford, UK
[b] Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College St., Toronto, Canada M5S 3E5

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ABSTRACT

Our severe dependence on fossil resources for the production of fuels and chemicals is responsible for two major global challenges: declining the fuel supply and increasing the anthropogenic greenhouse gas emissions. Conversion of biomass to fuels and chemicals can be a part of the low-carbon solution to both issues. Among various biomass species, inedible biomass such as lignocellulosics is the preferred choice for such applications due to their minimal impact on the food security. While technologies for the conversion of carbohydrates to value-added materials such as pulp, sugar monomers, and ethanol are well-established, lignin upgrading and valorization processes are significantly less-developed, and technical lignins are almost entirely burnt to generate heat and steam. The economic viability of biorefineries – which will receive significant amounts of lignin in future – can potentially improve significantly when advanced technologies are available that aid the conversion of lignin to value-added compounds. In this paper we assess how thermochemical processes can be used to isolate lignin from the lignocellulosic biomass, and subsequently convert it to liquid fuels, hydrogen, and aromatic monomers. To this end, different depolymerization, gasification and upgrading technologies for lignin conversion will be considered. Finally, the foreseeable applications of lignin-based products, the future directions for development, and the potential supportive interventions from policy makers are critically assessed.

Contents

* Corresponding author at: Smith School of Enterprise and the Environment, University of Oxford, 75 George St., OX1 2BQ, Oxford, UK. Tel: +44 7733 73992.
E-mail addresses: pooya.azadimanzour@utoronto.ca, pooya.azadi@gmail.com (P. Azadi).

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1. Introduction

The global population is growing and is likely to reach 10 billion by the end of the century with potentially devastating consequences for our environment and living quality. It will be increasingly difficult to provide food [1–3] and energy [4] for such a dense population, especially since the both energy and food provision is projected to increase per capita. For instance, average calorie supply per person in the developing world should be increased so that the global average reaches 3000 cal per capita and day (Fig. 1). Moreover, it is anticipated that a significant amount of energy provided comes from biomass. One crucial question that has to be asked when assessing biofuels is how the large-scale production will affect land use, water as well as food security and the risk of other detrimental environmental impacts. Combining the increased food supply with increased biofuel provision for an ever-growing population is non-trivial given a restricted global landmass and water supply [3].

The solution to this non-trivial problem is multifaceted: firstly, marginal and desert land has to be utilized as farmland for energy feedstock such as algae and agave. Secondly, marginal and degraded land has to be utilized to grow energy crops such as perennial grasses (which are mainly lignocellulosic). Thirdly, leftovers for instance from food production, paper production and forestry have to be utilized, analog to municipal solid waste, which has to be utilized as well. All of these processes produce lignocellulosic biomass either as byproduct or main product. Consequently, the efficient conversion of lignocellulosic biomass to energy will be critical to address the emerging food versus fuel dilemma for an ever increasing global population while minimizing environmental degradation. Efficient conversion especially of lignin is, however, itself not trivial.

Lignin, along with cellulose and hemicellulose, is one of the principal components of the lignocellulosic biomass which constitutes 15–35% of the weight and carries the highest specific energy content of all the three fractions [5–7]. Therefore, economic viability of the future lignocellulosic biorefineries depends upon conversion of both cellulose and lignin to value-added compounds. Lignin is a cross-linked amorphous copolymer synthesized from random polymerization of three primary phenylpropane monomers which are bonded together through several different C–O–C and C–C interunit linkages. The role of lignin in biomass is to provide the plant with structural integrity, water-impermeability, and resistance against microbial decay [6].

Although lignin holds great potential as a renewable source of fuels and aromatic chemicals, lignin valorization technologies are substantially less developed than those for the polysaccharides. Difficulties in catalytic processing caused by the existence of a variety of different interunit linkages, high affinity for the formation of a more condensed structure when thermochemically processed, poor product selectivity, and ease of use as a solid fuel are the major barriers towards the development of a lignin-based biorefining technologies. Owing to the massive amounts of lignin available in the pulp mills and in future biorefineries, establishment of lignin conversion processes will open a new route for the production of low-carbon biofuels and the currently fossil-based aromatics and will, in turn, improve the economic viability of the plant. One should refer to [8] for a discussion on relative economic advantages of various lignin-derived products.

In this paper, we first discuss the utilization of biomass, and lignin in particular, as a sustainable source for fuel production in terms of its availability and impact on the environment. Subsequently, the structure of lignocellulosic biomass and lignin is briefly overviewed. Then, the thermochemical processes by which lignin

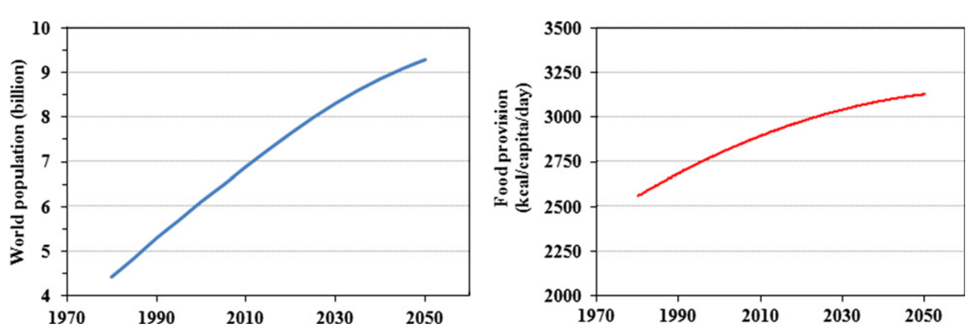


Fig. 1. United Nations Population Growth Extrapolation (left) and food supply estimated by FAO (right).

can be isolated from the biomass are discussed. The valorization of lignin through depolymerization and gasification are presented in the subsequent sections. Finally, the application of lignin-derived compounds as biorenewable fuels and aromatic chemicals are discussed in detail. More emphasis has been given to the production of lignin-derived solvents suitable for biomass processing which, if implemented, strengthens the economic competiveness of the biorefineries.

2. Availability and impact on the environment

In order to provide significant amounts of energy while minimizing social and environmental impact, feedstock for any type of biofuel have to fulfill certain prerequisites: firstly, feedstock has to have a high land-use efficiency, i.e. the amount of energy produce per area has to be high in order to produce significant amounts of fuel without impacting global land use. For instance, algae could potentially produce 850 GJ of bioenergy per hectare per annum (GJ/ha/a) compared to a 57 GJ/ha/a for U.S. corn ethanol [9,10]. Secondly, feedstock has to have a low water footprint, i.e. the water needed especially irrigation water has to be minimal per energy produced (low L/GJ). This prerequisite is essential in order to mitigate strain that biomass production can put on local water supply. A striking example for such a feedstock is agave which grows on arid, water-restricted land while producing significant amounts of useable biomass [11]. Thirdly, other detrimental effects on the environment have to be minimized: such as emissions from land-use change when creating new cropland [12,13], fertilizer use [14] and the carbon footprint of the biomass itself [10]. Last but certainly not least, it has to be ensured that biomass production does not – directly or indirectly – interfere with food production.

Table 1
Average organic constituents of some biomass feedstocks.

Feed	Cellulose	Hemicellulose	Lignin	Ref.
Softwood	40–44	20–32	25–35	[15]
Hardwood	40–44	15–35	18–25	[15]
Switchgrass	37	29	19	[17]
Wheat straw	38	29	15	[17]
Corn stover	38	26	19	[17]
Miscanthus	43	24	19	[17]
Eucalyptus	49	21	18	[18]
Agave	78	6	13	[18]
Bagasse	49	31	19	[18]

Feedstock such as agave or algae [9,11] fulfill all above prerequisites, they minimize environmental impact, have limited freshwater needs and produce significant amounts of bioenergy while not requiring arable land or fertilizer. However, these crops are only at the pilot stage and will not impact biomass availability in the short-term. In contrast, lignocellulosic biomass is available in the short term and fulfills the prerequisites as well. Leftovers from agriculture, forestry and from paper/pulp production are widely available and converting them into energy provides one with significant potential for producing bioenergy. Moreover, there is ample potential for harvesting energy crops such as perennial grasses on marginal land and utilizing municipal solid waste (MSW) that contains up to 40% lignocellulosic biomass [15] as a source of bioenergy and hence, avoiding land-fill. However, to make it economic to convert lignocellulosic biomass to useable biofuel, the process has to be optimized.

This review sets out the state-of-the-art for the conversion of the lignin fraction of lignocellulosic biomass, and points out where improvement is needed in order to convert it into useable biofuel of any type. In addition, the potential of fuel production from lignin given all the described hurdles are taken will be critically examined. Such assessments help with developing better informed policy and strategies for biofuel production.

3. Lignin chemistry and structure

3.1. Lignocellulosic biomass

Lignocellulosic biomass is mostly cell wall material that is composed of three principal components: cellulose, hemicellulose, and lignin (Table 1). Lignin constitutes 15–35% of the dry lignocellulose and it is the largest renewable source of aromatics on earth. As depicted in Fig. 2, the cell wall is comprised of several layers in which lignin concentration systematically decreases from the outer layer to the inner layer. Lignin in the outmost layer serves as a binding agent to hold the adjacent cells together whereas the lignin within the cell walls gives rigidity through chemical bonding with hemicellulose and cellulose microfibrils [16]. Additionally, lignin offers several unique characteristics such as resistance to decay and biological attacks, UV absorbance, and water impermeability. The heating values of the lignocellulosic biomass species vary linearly with the associated lignin content according to the following equation [17].

$$HHV\ (MJ/kg) = 0.0893\ L\ (\%) + 16.97 \quad (1)$$

where HHV and L represent the higher heating value (MJ/kg) and the corresponding lignin content (wt%) in the biomass, respectively.

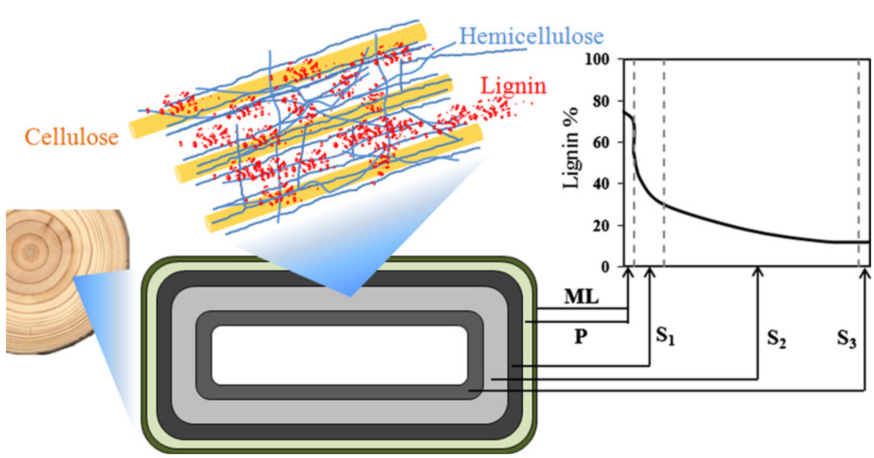


Fig. 2. Ultrastructure of wood cell wall and schematic diagram for lignin distribution within the middle lamella (ML), primary wall (P), and secondary wall (S_1, S_2, S_3) layers. The thicknesses of the layers in softwood are approximately 0.1 µm for S_1 and S_3, and 0.6 µm for S2 [16].

3.2. Lignin structure and interunit linkages

Lignin is a cross-linked amorphous copolymer synthesized from random polymerization of three primary phenylpropane monomers: coumaryl, coniferyl, and sinapyl alcohols containing zero, one, and two methoxyl groups, respectively. As listed in Table 2, both lignin content and the ratio between these primary monomer units vary among different plants and species. The lignin content of biomass decreases with the following order: softwood > hardwood > grasses. The softwood lignin is primarily

Table 2
Lignin content and chemical structures of three primary monomers of lignocellulosic biomass.

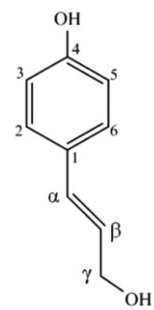
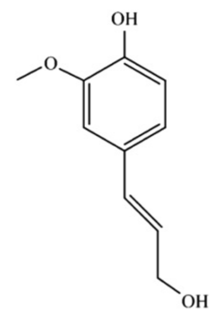
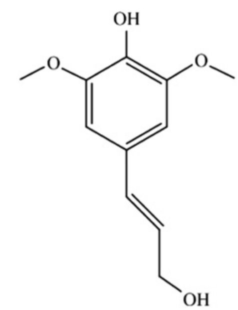
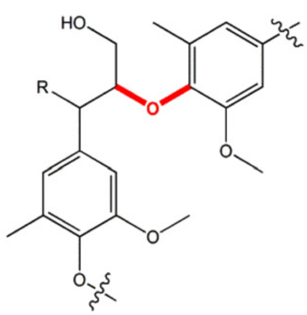
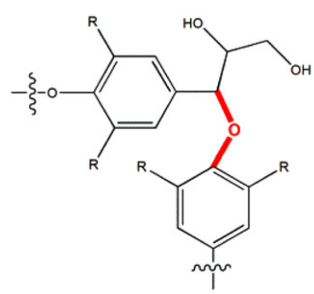
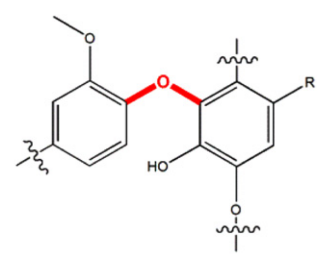
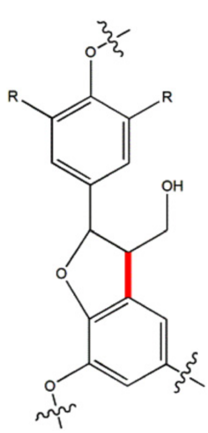
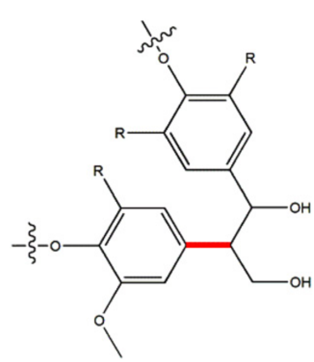
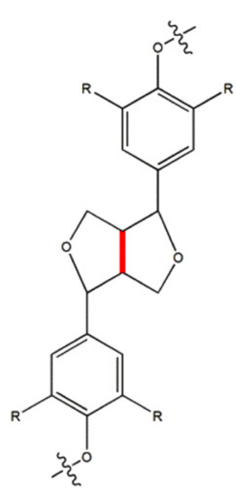
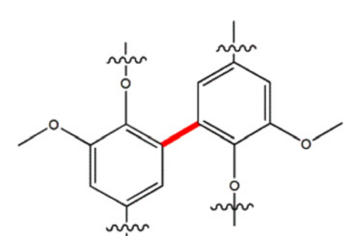
	Lignin (wt%)	**Phenylpropane unit (%)**		
Structure		 Coumaryl	 Coniferyl	 Sinapyl
Softwood	27–33	–	90–95	5–10
Hardwood	18–25	–	50	50
Grasses	17–24	5	75	25

Table 3
Proportions of interunit linkages for hardwood and softwood lignins.

C_9–O–C_9				
Linkages	*β*-O-4	α-O-4	4-O-5	
Softwood (%)	46	6–8	3.5–4	
Hardwood (%)	60	6–8	6.5	
C_9–C_9				
Linkages	*β*−5	*β*−1	*β*–*β*	5–5
Softwood (%)	9–12	7	2	9.5–11
Hardwood (%)	6	7	3	4.5

formed from coniferyl alcohol (guaiacyl structure), whereas almost equal amounts of coniferyl alcohol and sinapyl alcohol (syringyl structure) constitute hardwood lignins.

Generally more than two-thirds of the linkages in lignin are ether linkages. Hardwood lignin contains roughly 1.5 times more β-O-4-linkages compared to that of softwood. There are various functional groups in the structure of lignin including methoxyl, phenolic hydroxyl, aliphatic hydroxyl, benzyl alcohol, noncyclic benzyl ether and carbonyl groups which result in reactivity of the lignin in various chemical reactions.

The most frequent coupling linkages in the polymerization process are β-O-4-aryl ether bonds. The other major linkages include β-5-phenylcoumaran, 5–5-biphenyl, 4-O-5-diaryl ether, β-1-(1,2-diarylpropane), β-O-4-aryl ether, and β–β-resinol linkages which are depicted in Table 3 [7]. The proportions of these linkages vary significantly in various woods and plants. The approximate percentages of major linkages in hardwood and softwood lignin are also included in Table 3.

3.3. Lignin characterization methods

Due to the complex structure, inherent variation in the protolignin, and significant structural changes occurring by different the isolation methods, characterization of lignin has been a controversial subject over the past few decades. Here, we briefly overview the major methods for the determination of total lignin, molecular weight, and functional groups and readers should refer to [6,18–20] for a more detailed discussions regarding these methods.

The most widely used method for the determination of the lignin content of a lignocellulosic material is the Klason procedure. In this method, the carbohydrates present in the material are completely dissolved in a 72% concentrated sulfuric acid solution at room temperature followed by dilution of the solution to 3% and boiling for few hours to precipitate lignin. The acid-insoluble lignin is filtered off, dried and weighted [21]. The amounts of acid-soluble lignin for softwoods and hardwoods, which can determined by spectroscopic methods, are below 0.5% and 5%, respectively [21]. Due to its aromatic nature, lignin has strong UV absorption at 280 nm, while carbohydrates are transparent near such wavelength, rendering UV absorption a proper method for the quantitative measurements of lignins in solutions [6].

In all isolation processes, the protolignin in biomass is broken down into smaller fragments. An important attribute for the development of lignin-based products is the molecular weight and polydispersity of these lignin fragments. The most widely method for the determination of the molecular weight of lignin is gel permeation chromatography (GPC) performed on acetylated lignins dissolved in THF. However, acetylation of lignosulfonates and carbohydrate-containing lignins may lead to erroneous molecular weight data. Other methods used for such purpose include matrix-assisted laser desorption ionization/time of flight (MALDI-TOF) [6,18,22], size exclusion chromatography combined with multi-angel laser light scattering (SEC-MALLS) [23], and vapor pressure osmometry (VPO) [24].

Spectroscopic methods namely NMR, FTIR and UV absorption has been extensively utilized to shed light into the complex structure of lignin. The assignment of infrared absorption bands and 1H and 13C shifts for several model compounds of lignin are available in [20] and [25], respectively. Also, degradative techniques are used to quantify the methoxyl, phenolic hydroxyl and carbonyl functional groups of lignin.

4. Lignin isolation processes

There are several different methods by which lignin can be isolated from biomass. These processes can be classified into two general groups: (i) processes in which lignin is degraded into soluble fragments and is removed by separating the solid residue from the spent liquor and (ii) processes that selectively hydrolyze polysaccharides and leave lignin along with some condensed carbohydrate deconstruction products as a solid residue. The example of former would be all pulping processes: such as kraft, sulfite, soda, and organosolv, and an example of the latter would be dilute acid hydrolysis of lignocellulose to yield sugar monomers, furfural and levulinic acid. Regardless of the process utilized, lignin usually undergoes significant structural changes during the separation from other components and hence, the behavior of the isolated lignins can be substantially different from the native lignin in wood. In addition to the structural changes caused by severe lignin isolation conditions, sulfur is incorporated in the structure of lignin obtained from kraft and sulfite pulping processes which are currently the most commonly used pulping processes.

It should be noted that the isolated lignins are typically a complex mixture of several different phenolic compounds with a varying degrees of polymerization from one to hundreds. Regardless of the pulping process utilized, it has been found that the polydispersity (Mw/Mn) of the isolated lignin fragments can be approximated from the following equation [26]:

$$M_w/M_n = 4.5 \times 10^{-4}(M_w) + 0.85 \quad (2)$$

where M_w and M_n are the weight and number average molecular weights. Here, we give an overview of the current and emerging technologies for the lignin isolation and discuss the characteristics of the resulting lignins with regard to their potential for further valorization. One should refer to [27] for more detailed information regarding different pulping processes.

It has been suggested in the literature that the Milled Wood Lignin (MWL), also referred to as Björkman lignin, has the most structural similarities with the protolignin in the non-fractionated biomass which renders it suitable for analytical studies. Briefly, MWL is obtained from disintegration of pre-extracted wood in a neutral solvent such as toluene at the room temperature using a vibratory ball mill.

4.1. Kraft process

The kraft (sulfate) pulping (Fig. 3) is the dominant global pulping process with about 90% share of the total production capacity. In this process, cellulose fibers are isolated through dissolution of lignin and hemicellulose of the wood chips in a solution of sodium hydroxide and sodium sulfide (i.e. white liquor). The initial pH is adjusted between 13 and 14 but it gradually decreases over the course of digestion as a result of the liberated organic acids from hemicellulose and lignin. After a predetermined exposure to the cooking liquor at temperatures around 170 °C, the dissolved organics and the inorganic chemicals used for pulping leave the digester as an aqueous stream with

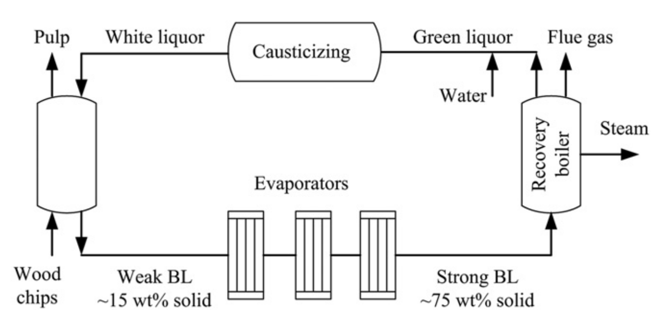


Fig. 3. A simplified flow diagram of the kraft pulping process.

about 15% solid content (i.e. weak black liquor). In this process lignin dissolution occurs owing to the reaction between hydroxide and hydrosulfide anions which consequently results in the formation of alkali-soluble fragments. Generally, lignin encounter two types of reactions during pulping: (i) degradation reactions which result in smaller lignin fragments and enhance the solubility in water/alkali solution and (ii) condensation reactions which form alkali-stable linkages and decrease the digestion efficiency. The lignin content of the black liquor varies from 29 to 45% for cook of paper grade and 8–16% for liner grade cook [28]. The lignin content of kraft black liquor from softwood is typically higher than that of hardwood. Also, it is widely accepted that owing to these severe degradation and condensation reactions, the native lignin undergoes dramatic chemical and structural changes. For instance, the percentage of refractory C–C linkages between the propyl phenol monomers is significantly higher than in the protolignin initially presented in the wood [29], making it very difficult to depolymerize the kraft lignin in the subsequent processes. Although kraft lignin can be recovered by acidification of the black liquor in high yields, very few kraft mills (i.e. 2% [6]) made commercial kraft lignin for sale and majority of the mills burn the organic content of black liquor in recovery boilers for the production of electricity and steam. The acidification process for the isolation of kraft lignin from the other wood degradation products in black liquor is carried out by mineral acids or carbon dioxide [6]. The kraft (alkali) lignin typically contains little sulfur in its structure (i.e. 1.5–3 wt% [30]) which is significantly lower than that of the lignin obtained from sulfite pulping (i.e. 4–8% [6]). Nonetheless, since kraft lignin is only soluble at $pH > 10$, most of the commercially available kraft lignin is sulfonated to become water soluble [6]. The sulfonation of precipitated kraft lignin is carried out using sodium sulfite at temperatures below 200 °C. Due to lack of a reliable methodology for the measurement, determination of the molar mass of lignin is a controversial topic; however, the average molar mass of kraft lignin is consistently reported to be below 10,000 Da, corresponding to a degree of polymerization of approximately 50 and smaller [6]. The heating value of the degraded lignin and hemicellulose in the black liquor is substantial (e.g. 14–16 MJ/kg on a dry basis [31]). Therefore, the value of any chemical to be produced from the lignin fraction of the black liquor should be adequately high that it compensates for the cost of the capital installation and of the additional fuel required to replace the removed lignin.

4.2. Sulfite pulping

As kraft process has become the dominant pulping process all around world, the importance of sulfite pulping has dramatically decreased and only about 10% of the pulp is currently produced by this method [27]. The sulfite process is extremely flexible in terms of pH range and in principle it can be operated over the entire pH range (i.e. 1–13) simply by changing the pulping chemicals and adjusting the dosage. Sulfite pulping is based on the use of aqueous sulfur dioxide as well as calcium, magnesium or sodium as the counter ion. The digester is typically operated in a temperature range of 120–180 °C with a digestion time of 1–5 h [27]. The major reaction that occurs during the sulfite pulping is sulfonation of lignin through the introduction of sulfonic acid to the α-carbon atoms, which subsequently lead to the hydrolysis of the lignin. The degree of sulfonation per unit phenylpropane monomer in the commercial lignosulfonates varies between 0.4 and 0.7 [23] and it decreases by increasing the molecular weight of the lignosulfonate fraction [32]. In contrast to alkali lignin, the sulfur content of lignosulfonates obtained from sulfite pulping is rather high (i.e. 4–8%), making lignosulfonates soluble over almost the entire pH range. Also, the average molar mass of both sulfonated lignin fragments as well as the molar mass of the phenolic monomers of lignosulfonate is higher than that of the kraft lignin [6,7]. It is important to note the average molecular weight of lignosulfonate from softwood (e.g. ~60,000) is significantly higher that of the lignosulfonate from hardwood (e.g. ~12,000).

4.3. Sulfur-free alkali (soda) pulping

Pulping of annular plants by soda pulping process accounts for nearly 5% of the total pulp production [27]. Typical feedstock used in soda pulping includes agricultural wastes such as bagasse and straw as well as the cultivated fiber plants such as kenaf and hemp. Due to lower lignin content, only 10–15% NaOH based on the raw material is required for delignification. It has been shown that the addition of catalytic quantities of antroquinone (AQ) has a marked effect on stabilization of carbohydrates and dissolution of lignin; however, the rate of lignin removal is still lower compared to the kraft process. It is expected that soda or soda/AQ pulping may become more important in the context of biorefineries because firstly, the spent liquor and hence the precipitated lignin will essentially be sulfur-free, and secondly, the annual plants are inherently easier to delignify and the lower delignification rates would be somewhat tolerated for these species. It should be highlighted that the presence of sulfur in the structure of kraft and sulfite lignins has always been a barrier against a more effective utilization of the lignin in the downstream catalytic processes. Moreover, gasification of kraft black liquor leads to a partial or full partitioning of sulfur to the gas phase which in turn causes gas separation issues and more importantly, a higher causticizing demand for chemical recovery due to lower sulfur to sodium ratio in green liquor. The molecular weight of some soda/AQ lignins are given in Table 4. It was shown that a soda lignin from bagasse with an average molecular weight of 2400 can be fractionated into three parts: diethyl ether soluble (~8%, M_w=560), methanol soluble (~68%, M_w=2700) and solid residue (24%, M_w=6000) with carbon contents of 70%, 64% and 44%, respectively [33]. Due to the absence of sulfur in their structure, the molecular weights of the C_9 monomers of soda lignin are typically lower than that of kraft and sulfite lignins [34].

4.4. Organosolv processes

The term "organosolv" refers to a group of pulping processes based on low-boiling organic solvents. Majority of these processes utilize sulfur-free chemicals for delignification. The most commonly used solvents for organosolv delignification include alcohols such as methanol and ethanol (usually with ~50% water), organic acids such as formic and acetic acid and mixed organic solvent–inorganic alkali chemicals. The use of high-boiling solvents for organosolv pulping allows for the operation of the process at the atmospheric pressure but would be more difficult to recover from the spent liquor [35]. One of the main derives for developing organosolv pulping was their more environmentally benign pathway compared to kraft and sulfite processes. Moreover, some organosolv processes can essentially isolate cellulose,

Table 4
Characteristics of soda lignin obtained from different biomass species.

Feed	AQ	OCH3 per C_9	Mw	Mn	Mw/Mn	Ref.
Alfa grass	–	1.1	10,400	1770	5.9	[36]
Softwood	✓	1.4	5500	1260	4.3	[37]
Flax	✓	1.8	2600	1500	1.8	[38]
Bagasse	–	0.7	2410	2160	1.1	[34]
Long fiber plants	✓	1.2	1300	650	2.0	[35]

hemicellulose and lignin fractions which in turn allows for implementation of a more specific downstream process on each fraction and hence, improving the economical viability of the biorefineries. It is important to note that owing to its sulfur-free and less-condensed structure, the organosolv lignin is one of the most suitable types of technical lignin for further conversion and valorization. In spite of these advantages, none of the organosolv pulping technologies has been yet widely adopted in a production-scale mill [36]. However, thanks to the great potential of organosolv lignins and the ever rising concerns over the environmental impact of traditional pulping processes, it is anticipated that the organosolv methods will find more interest in the future for biomass fractionation. Figs. 4 and 5 show the rising research activities with regard to organosolv methods as represented by the number of annually published papers.

4.4.1. Alcohol organosolv processes

The Alcell process, one of the most extensively developed organosolv processes, utilizes 50% ethanol solution for delignification of hardwood in a series of extractors operated at 190 °C and 28 bar [37]. After loading the wood chips into each digester, the vessels are purged with steam and cooked by the circulation of the primary liquor which was previously used as secondary liquor in the previous cook. After about an hour, the spent primary liquor containing dissolved lignin, hemicellulose oligomers, and furfural is drained from the extractor and sent to the product recovery section. Since no mineral acid or alkali is used in the Alcell process, the spent liquor is only slightly acidic (i.e. pH=4) due to the release of acetic acid from hemicellulose. Following this step, the extractors are loaded with the secondary liquor which already contains small amounts of dissolved organics as it was used as the last wash in the previous cook. After an appropriate exposure time, the used secondary liquor is drained from the extractors and kept in an accumulator to be used in the next cook as primary liquor. Finally, the recovered alcohol (with no dissolved solid) is contacted with the cook as the tertiary liquor after which it is sent to the secondary accumulator. The spent primary liquor which contains ethanol, water, soluble lignin fragments, carbohydrates (e.g. xylose) and furfural from hemicellulose is fed to a flash drum where ethanol is partly recovered through the condensation of the overhead vapors. Following the partial removal of ethanol, Alcell lignin is separated through a clarifier and centrifuge as precipitates. The liquor left in clarifier is further separated into its constituents in a distillation column where more ethanol is recovered from the top of column, furfural is obtained as side draws and the dissolved carbohydrates and lignin-derived phenolic monomers are collected as bottoms. These organics can be subsequently separated and used as chemicals or burnt to provide heat for the process. The heating value of Alcell lignin is reported at 25.5 MJ/kg [37]. Alcell lignin is highly soluble in acetone, THF, and ethylacetate and it is insoluble in water [38]. The average molecular weight (Mw) of Alcell lignin obtained from hardwood is reported at 3300 Da with a polydispersity of 3.7.

While a variety of different auto-catalyzed and acid-catalyzed organosolv processes has shown promise for pulping of hardwoods, they often fail to produce softwood pulp at reasonable yields and acceptable strengths. In order to address this issue, a few number of alkali-organosolv processes have been proposed, among which the Organocell process received major development activity. In this process, wood delignification is performed in two successive stages. In the first stage, wood chips are impregnated with 50% methanol solution at 170–190 °C for 20–40 min. Subsequently, the partially delignified wood chips are fed to a digester where methanol concentration is decreased to 35% and sodium hydroxide is added to the liquor to facilitate dissolution of the remaining lignin. The second stage of the Organocell process is typically operated at 170 °C and 40–60 min residence time. It has been shown that about 50% of the organics dissolved at the onset of digestion of softwood in the first stage of Organocell pulping is non-lignin compounds (i.e. extractives and carbohydrates), but this ratio rapidly drops to about 10% after 40 min. Analysis of the chemical structure of the Organocell lignin from the second stage indicated almost the same number of methoxy functional groups per C_9 unit (i.e. 0.94) compared to milled wood lignin of the same softwood species [39]. Organocell lignin can be obtained by evaporation of methanol followed by acidification with phosphoric acid to pH=4. The structure of Organocell lignin is more altered than the lignins from auto-catalyzed or acid-catalyzed organosolv processes such as Alcell [40], but the sugar content of the Organocell lignin is found to be rather low (e.g. < 2 wt%) [39]. The average molecular weight of Organocell lignin obtained from the second stage is reported at 4100–11,000 [26,24]. For each specific cook, the molecular weights of the samples taken within each stage show a negligible variation with time [24]. Also, the average molecular weight of lignin from the first stage is consistently lower than that of lignin from the second stage. Accordingly, monomer yields of 9.5% and 1.6% are reported for the lignins from the first and second stages, respectively [24]. In summary, the byproducts of the Organocell pulping process, including the Organocell lignin, are less suitable for further conversion to value-added chemicals except for the syngas generation through gasification. Alternatively, sodium hydroxide could be recovered from the spent liquor in a process similar to the conventional black liquor recovery process in kraft pulping where sodium hydroxide is recovered through recausticization.

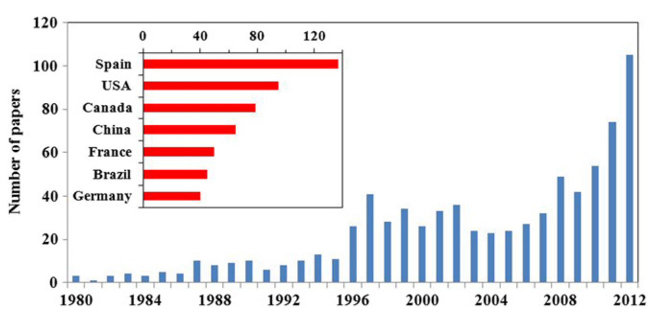


Fig. 4. Number of papers published on organosolv biomass fractionation since 1980 and the breakdown from the top contributors. Data extracted from Scopus.

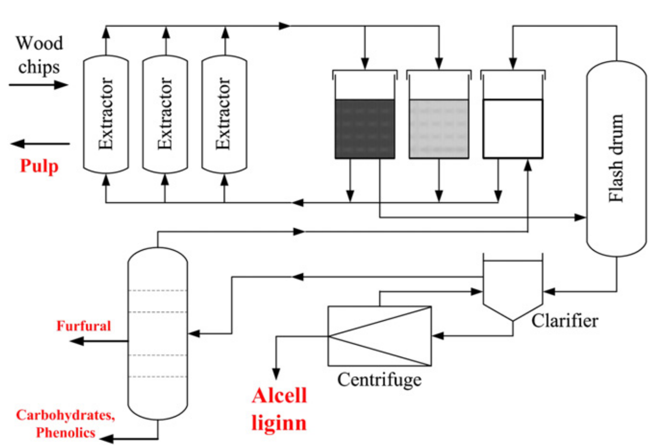


Fig. 5. A simplified process diagram of Alcell organosolv pulping, adapted from Ref. [41].

4.4.2. Acid organosolv processes

Delignification of wood in organic solvent is facilitated at higher hydrogen ion contents. It has been demonstrated that formic acid and acetic acid are fairly suitable for the cleavage of lignin α-ether linkages and dissolving the subsequent lignin fragments at low to moderate temperatures. Low temperature pulping is carried out at atmospheric or low operating pressures but requires peroxides or catalyst such as HCl [27]. Delignification in presence of formic acid was found to proceed faster than in presence of acetic acid [41]. The lignins recovered from organosolv pulping of Eucalyptus globulus with acetic acid showed higher methoxy content compared to that of formic acid [42].

High concentration formic acid solution with or without the addition of hydrogen peroxide and mineral acid can be used to fragment and dissolve lignin. Formic acid is expected to be readily available in biorefineries from conversion of C6 sugars to 5-hydroxymethylfurfural (HMF) followed by acid hydrolysis to levulinic acid and formic acid. The operating temperature and digestion time for delignification of wood using concentrated formic acid solution is typically 90–120 °C and 30–90 min [43–45]. Milox is a three stage pulping process based on formic acid which employs hydrogen peroxide in the first and third stages to give rise to peroxyformic acid [46]. The reaction temperature in the first and third stages is 80 °C while it is increased to 100 °C in the second stage. Softwood, hardwood and non-woody plants can be delignified in Milox process [47]. Treatment of siam weed stem according to Milox process resulted in a low-molecular weight lignin (M_w=2100) with 1.26 methoxy (–OCH3) functional group per unit C_9.

A few number of acetic acid-based organosolv pulping processes have been developed and patented. Among them, the processes listed in Tables 5 and 6 received great deals of attention.

Xylan and xylose are readily dehydrated to furfural in high yields (up to 80% of the theoretical value) in organic acid solutions that are used in acetic acid organosolv processes [48]. The order of conversion of pentose to furfural in acetic acid pulping processes decreases with the following order: Acetosolv > Formacell > Acetocell. The same order, though substantially at lower values, for the conversion of C6 sugars to hydroxymethylfurfural (HMF) and Acetoxymethylfurfural (AMF) were observed [48]. Moreover, the Acetosolv was found to be more corrosive compared to Formacell and Milox processes [49].

Table 5
Operating condition and liquor composition of acetic acid-based organosolv processes.

Process	Acetic acid wt%	Water wt%	Co-solvent or catalyst	Temperature (°C)
Acetosolv	> 90	< 10	0.05–0.2% HCl	90–110
Formacell	50–95	0–45	5–10% formic acid	160–180
Acetocell	80–90	10–20	–	170–190

Table 6
Characteristics of lignins obtained from acetic acid organosolv pulping processes.

Feed	AC%	Percentage of HCl	T (°C)	M_w	M_n	M_w/M_n	Ref.
Miscanthus giganteus	90	0.15	116	6020	1440	4.2	[52]
Wheat straw	90	0.10	85	3960	2330	1.7	[53]
Hardwood	85	–	185	3200	–		[54]
Siam weed stem	93	0.1	103	2010	710	2.8	[55]
Bagasse	90	0.1	110	1710	990	1.7	[56]

4.5. Fast pyrolysis of lignocellulose

Fast pyrolysis is a thermochemical process that converts dry biomass to a liquid product known as bio-oil, as well as char and gas in the absence of oxygen and steam. Fast pyrolysis is typically carried out at temperatures near 500 °C and atmospheric pressure with a residence times of less than 2 s. The product distribution in terms of bio-oil, solid char and gas is primarily dominated by the reaction temperature, the heating rate and the lignin content of the feed. Virtually any type of biomass can be used as a feedstock to the pyrolysis process provided that its moisture content is low. Different reactor configurations such as fluidized bed and circulating fluidized bed with inert solid particle heat carriers have been implemented to ensure fast and uniform heating which is essential for obtaining high bio-oil yields. It should be realized that pyrolysis process may be employed for two different purposes within the context of lignin valorization: (i) production of pyrolytic lignin and carbohydrate-derived bio-oil phases from the non-fractionated lignocellulose and (ii) decomposition of lignins obtained as a byproduct of other lignocellulose fractionation processes.

There is a large body of literature on the fast pyrolysis of lignocellulosic biomass as a whole. In addition to breaking down the large biomass molecules into smaller fragments, pyrolysis can be also considered as a method for separating the lignocellulosic biomass into carbohydrate (i.e. water-soluble) and lignin (i.e. water-insoluble) fractions. In this section, we briefly overview the methods by which the lignin-derived compounds can be separated from the bio-oil mixture obtained from lignocellulosic feedstock, and subsequently discuss the characteristics of these pyrolytic lignins. Pyrolysis of isolated lignins previously produced as a byproduct in other biomass fractionation processes and pyrolytic gas formation from lignin will be discussed in Sections 5.1 and 6.2, respectively.

The yield of bio-oil from pyrolysis of lignocellulose can be as high as 75%. The pyrolysis bio-oils consist of a large number of compounds that, to varying extents, retain some structural similarities with their original molecules. Accordingly, the higher affinity of the compounds obtained from the deconstruction of carbohydrates to water compared to that of the lignin-derived compounds allows for an easy separation of the two fractions. Addition of the bio-oil mixture to ice-cooled water at high water to oil ratios (e.g., 10:1) under vigorous agitation causes the pyrolytic lignin to precipitate as brown particles [8]. However, this method does not produce pure phases and cross-contamination in both portions of the separated bio-oil exists. The water-soluble fraction can be further upgraded to useful chemicals or reformed to produce syngas and hydrogen, the latter of which can be subsequently used for hydrogenolysis and hydrogenation of the precipitated lignin. The pyrolytic lignin is an attractive intermediate platform for lignin valorization as it is essentially free of sulfur and has relatively low molecular weight which renders it a suitable feed for further catalytic processing.

The yield of the brown powder, known as pyrolytic lignin, obtained from the abovementioned method can be as high as 28 wt%, indicating that a large fraction of lignin partitions into bio-oil upon fast pyrolysis of biomass. The elemental analysis of the pyrolytic lignins obtained from several different lignocellulosic species revealed that they are comprised of approximately 66% carbon, 6% hydrogen and 27% oxygen, almost independent of the original feedstock [50]. It is also important to note that the carbon content of the pyrolytic lignin is 9–15% and 3–9% higher than the corresponding values in the bio-oil and in milled wood lignin (MWL) obtained from the same feedstock, respectively [50]. As a result, the heating value of the pyrolytic lignin is significantly higher than the original bio-oil and the milled wood lignin.

Furthermore, FTIR analysis has revealed that the methoxyl groups of pyrolytic lignins are consistently lower than that of the native lignin represented by milled wood lignin, likely caused by demethoxylation of the guaiacyl and syringyl moieties to form methanol [50].The average molecular weight of the pyrolytic lignins were reported to be in the range of 650–1300 Da, corresponding to an average degree of polymerization of approximately 3–7 [51]. Expectedly, the average molecular weight of pyrolytic lignin increases by aging the bio-oil from which the lignin is precipitated [22]. It has been suggested that the pyrolytic lignins are comprised of some thermally ejected oligomers in addition to the newly formed structures through repolymerization, the former of which primarily consists of C–C bonded units that survived the pyrolysis conditions and latter of which consists of recombined compounds with functional groups at untypical positions [52]. Pyrolytic lignin can be also separated from the bio-oil using controlled deposition method [53] or solvent extraction [54,55].

4.6. Dilute acid hydrolysis

The Biofine process (Fig. 6), one of the most advanced lignocellulosic-fractionating technologies, is a two-stage high-temperature acid-hydrolysis process in which the polysaccharides are hydrolyzed to their monomeric constituents, and in turn, they are converted into valuable platform chemicals such as furfural from C_5 sugars and levulinic acid and formic acid from C_6 sugars. The lignin and ash constituents of the biomass form the solid residue called Biofine char which has a very high heating value (e.g. 26 MJ/kg [56]). FTIR spectra and thermogravimetric analyses have indicated that the Biofine char is mainly composed of ligneous type components.

4.7. Hydrothermal fractionation

Lignin along with hemicellulose can be partly separated from wood in hot-compressed water at temperatures near 200 °C under moderate hydrogen pressure and in the presence of a proper hydrogenation catalyst [57,58]. The role of catalyst in such process is to selectively hydrogenate and hence cleave the C_9–O–C_9 linkages between the phenolic monomers of the fragmented lignins. The primary monomeric products include guaiacyl propanol and syringyl propanol in varying ratios depending upon the type of the lignocellulosic feedstock and the reaction conditions. Meanwhile, the propanol moiety of these two monomers is partially hydrogenated to yield an aliphatic propane branch. Thus, the ultimate products of the process are a mixture of propyl guaiacol, propyl syringol, guaiacyl propanol, and syringyl propanol along with the hemicellulose hydrolysis products

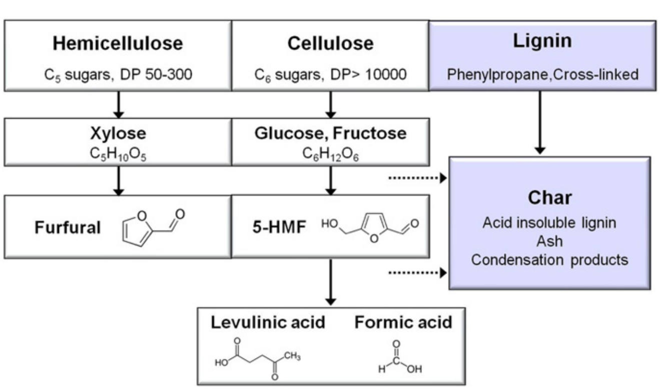


Fig. 6. Chemical transformations of cellulose, hemicellulose and lignin in the Biofine process.

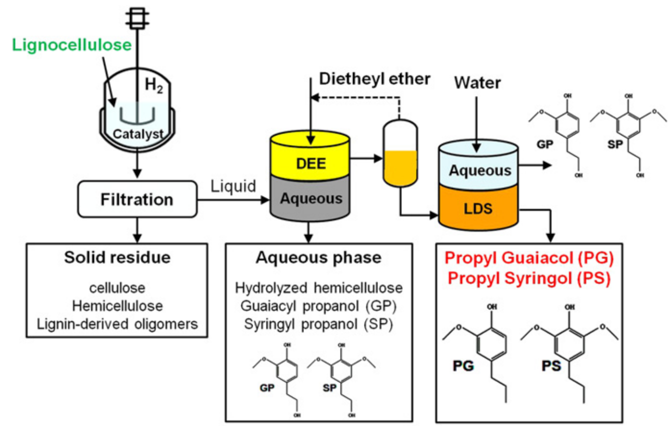


Fig. 7. Fractionation of lignocellulose and synthesis of hydrophobic lignin-derived solvent composed of propyl guaiacol (PG) and propyl syringol (PS) from hardwood in hot-compressed water.

remained in the aqueous phase (Fig. 7). The superior advantage of this process over other lignin isolation processes is its excellent product selectivity which allows for an effective utilization for various applications. However, separation of the heterogeneous catalyst from the wood residue seems to be quite challenging. Development of homogenous catalysts such as in [59] with the same function which can be easily separated from the solid residue can be considered as an alternative. Please refer to Section 5.1 for a more detailed discussion.

4.8. Biphasic fractionation

Biphasic aqueous systems can be used for in situ separation of the three principal components of biomass where the hemicellulose degradation products such as C_5 sugar oligomers and furfural are dissolved in the aqueous phase, the lignin fragments are extracted by the organic phase, and the cellulose remains as the solid residue, allowing for a full valorization of each fraction. Phenol [60–63], cresol [64], lignin-derived phenolic mixtures [65], polyethylene glycol (PEG) [66–70], and 2-methyltetrahydrofuran (MTHF) [71] have been applied as the organic phase. Acid or alkali can be added to the aqueous phase to facilitate the degradation of hemicellulose and lignin. Also, dissolution of mineral salts into the aqueous phase improves the degree of phase divergence in the spent liquor. Pulping with phenol–water mixture, also known as the Battelle–Geneva process, is operated at temperatures near 100 °C and atmospheric pressure with 40% phenol solvent [60,63]. The phase separation of the homogeneous phenol–water mixture at the pulping reaction condition occurs by cooling down the spent liquor. Use of oxalyic acid as the catalyst for fractionation of hardwood in MTHF-water system at temperatures near 140 °C results in a cellulose-rich solid residue, a xylose-rich aqueous phase, and a lignin-rich organic phase [71]. The obtained pulp is readily hydrolyzed to soluble oligomers and glucose by enzymatic treatment and the catalyst is recovered from the aqueous phase by crystallization. The characteristics of the lignins obtained from these biphasic fractionation methods have not been reported in the literature.

5. Depolymerization

Here, we overview the features of five lignin depolymerization processes, namely pyrolysis of the isolated lignins, catalytic hydrogenolysis, alkaline hydrolysis, supercritical water and solvent depolymerization, as depicted in Fig. 8. The hydrogenolysis

of non-fractionated lignocellulose has been addressed in Section 4.7. In general, lignin depolymerization can take place in aqueous phase, organic phase as well as in a dry form. In contrast to the hydrogenolysis of native lignin in the non-fractionated biomass, depolymerization of the isolated lignins results in a complex mixture of aromatic compounds in which the individual mass fraction of each compound barely exceeds few percent. Furthermore, the C–C linkages of lignin are significantly more resistant towards cleavage and majority of them survive regardless of the depolymerization process. Fig. 9 demonstrates the theoretical yields of monomers, dimers and oligomers (and polymers) that can be produced from hardwood and softwood upon the cleavage of a certain percentage of the C_9–O–C_9 linkages. In this calculation, the lignin content of hardwood and softwood were considered 20% and 25% and the total percentage of all aryl ether linkages were considered 75% and 57%, respectively. The monomer and dimer yields are equal to x^2L and $x^2(1\text{-}x)$L, respectively, where x is the ratio of broken linkages to the total linkages (both C–O–C and C–C) and L is the lignin content of the wood [57,58]. The results revealed that if only the C_9–O–C_9 linkages are broken, the cumulative yield of monomers will be higher than that of dimers, regardless of the technology employed. Also, it is noted that although softwood contains more lignin than hardwood, the maximum yield of monomers that can be obtained from softwood (i.e. ~81 g/kg wood) is significantly lower than hardwood (i.e. ~112 g/kg wood). Furthermore, one can expect that the softwood depolymerization products have lower methoxyl moieties on average.

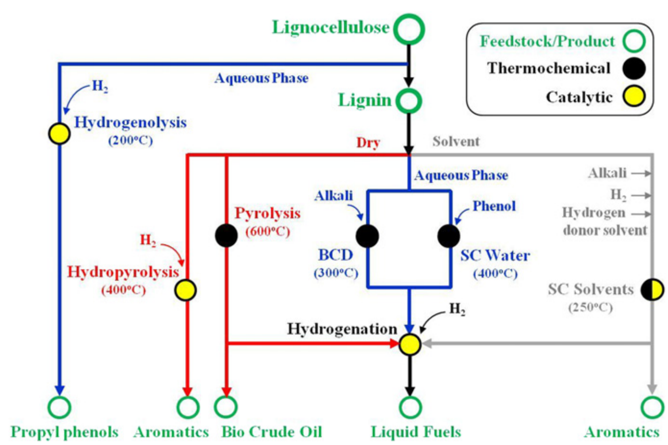


Fig. 8. Lignin depolymerization processes and products. Numbers in parentheses represent typical operating temperatures. (SC: supercritical, BCD: Base-catalyzed depolymerization).

5.1. Pyrolysis of isolated lignins

Pyrolysis of the isolated lignins is considerably different from the pyrolysis of wood and other lignocellulosic materials both in terms of the bio-oil composition and the product distribution over bio-oil, char, and gas. Therefore, one would also expect that the pyrolysis conditions such as the temperature and the residence time for the conversion of isolated lignins should be separately optimized for each feedstock from different biomass species and isolation processes (e.g., kraft, organosolv, pyrolytic, etc.). Thermogravimetric studies have revealed that lignin pyrolysis occurs over a wider range of temperature (e.g. 160–900 °C) compared to polysaccharides (e.g. 220–400 °C) [72]. Also, the amount of solid residue (i.e. pyrolysis char) from isolated lignins is significantly higher than the residue from carbohydrates or the non-fractionated biomass. The bio-oils obtained from the pyrolysis of isolated lignins are complex mixtures of many aromatic and non-aromatic compounds, each of which typically constitutes less than 1% of the total weight and with a wide molecular weight distribution from light hydrocarbons to high-molecular weight oligomers. It has been recently shown that the use of solid acid catalysts such as HZSM-5 in pyrolysis of lignin can effectively shift the product distribution towards more deoxygenated compounds [73–76]. The pyrolysis char has a low specific surface area (<5 m^2/g) [77] and the C/O and C/H ratios in the solid residue (pyrolysis char) increases by increasing the pyrolysis temperature [77,78].

Pyrolysis of various types of lignins obtained from major isolation processes have been reported in the literature; including alkali [72,75,77,79–83], organosolv [76,78–80,81,83–85], soda [85–87], acid hydrolysis [86,88], milled wood lignin (MLW) [80,89,90], steam explosion [80,87], pyrolytic [91], and enzymatic [78]. Selected results of these studies are presented in Table 7.

5.2. Catalytic hydropyrolysis

Dry lignin can be catalytically transformed into a liquid mixture at temperatures significantly lower than that of pyrolysis with the aid of hydrogen. Different terminologies have been used in the literature to refer to the catalytic processing of dry isolated lignin in high hydrogen pressures; such as hydropyrolysis, hydrocracking, hydrodeoxygenation, hydrotreating, and hydrogenolysis. A wide range of chemical reactions including the cleavage of the interunit linkages, deoxygenation, ring hydrogenation, and removal of the alkyl and methoxyl moieties of lignin proceed simultaneously, resulting in a complex oil mixture somewhat analogous to pyrolysis bio-oil. The lower oxygen content of the hydropyrolysis oil renders it more chemically stable than the bio crude oil from fast pyrolysis. It has been reported that hydrogen

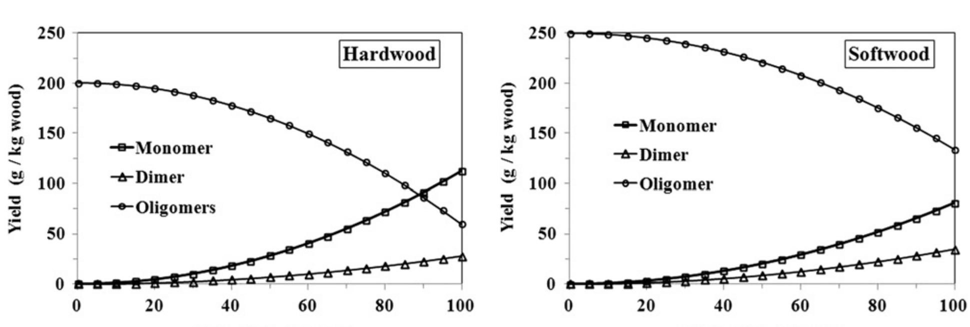


Fig. 9. Theoretical yields of monomers, dimers and larger oligomers formed upon cleavage of C_9–O–C_9 linkages. (Hardwood: 20% lignin, 75% C_9–O–C_9 linkage, softwood: 25% lignin, 57% C_9–O–C_9 linkage).

Table 7
Lignin pyrolysis product distribution.

Lignin	T (°C)	Bio-oil (%)	Gas (%)	Char (%)	Ref.
Kraft	550	23	39	41	[89]
Kraft	700	44	18	38	[92]
Kraft	800	19	36	45	[93]
Lignosulfonate	550	40	15	45	[97]
Soda	530	31	6	49	[96]
Soda	650	70	15	15	[84]
Organosolv	500	16	3	81	[88]
Organosolv	550	16	21	63	[89]
Organosolv	550	34	14	33	[94]
Organosolv	560	52	28	19	[86]
Acid hydrolysis	500	58	10	27	[96]
Acid hydrolysis	650	63	20	17	[84]
Steam explosion	550	33	17	50	[97]
Pyrolytic lignin	600	32	10	58	[101]
Milled wood lignin	600	36	16	40	[99]
Enzymatic hydrolysis	500	24	7	69	[88]

Table 8
Selected results of catalytic and non-catalytic dry lignin hydropyrolysis.

Lignin	T (°C)	H_2 (bar)	Catalyst	Liquid (%)	Char. (%)	Ref.
Kraft	395	100	NiMo–Cr_2O_3	65	2	[104]
Kraft	400	100	Ni–Mo	62	<2	[102]
Kraft	430	90	–	22	42	[105]
Kraft	430	90	$(NH_4)_6Mo_7O_{24}$	61	1	[105]
Acetosolv	420	100	Ni–Mo	38	24	[102]
Organocell	380	100	–	15	~60	[102]
Organocell	380	100	Pd	81	~0	[102]
Organocell	395	100	NiMo–Cr_2O_3	71	7	[104]
Organocell	400	50	NiMo–Cr_2O_3	28	32	[103]
Organocell	400	140	NiMo–Cr_2O_3	80	<2	[103]
Pyrolytic	400	140	Co–Mo	64	<2	[106]

pressure strongly affects the oil yield [92,93]. The hydropyrolysis catalyst should ideally show the following attributes: (i) high activity for the hydrogenolysis and/or cracking of the C_9–O–C_9 and C_9–C_9 interunit linkages, (ii) low activity for the hydrogenation of the benzene ring and the substitute alkyl and methoxyl groups which imposes an excessive hydrogen consumption, (iii) meaningful selectivity (e.g. $>10\%$) towards a certain compound or a class of compounds with a narrow boiling points to allow for an effective product separation, (iv) high resistance against coke formation and ease of regeneration to remove the catalyst from the solid residue, (v) high sulfur resistant if processing kraft or lignosulfonate lignins in which case sulfur will remove as H2S. Bifunctional catalysts which comprised of an active hydrogenation metal and acidic supports such as zeolites to selectively open some C–C bonds can potentially fulfill these requirements. The use of semicontinuous reactors in which hydrogen is passed through a bed of lignin and catalyst mixture allows for an in-situ removal of the desirable products (i.e. light oil) and avoids the undesirable secondary reactions [93]. Selected results from catalytic hydropyrolysis of some technical lignins are given in Table 8. For the sake of comparison, results of few non-catalytic experiments but with relevant reaction conditions are also included.

5.3. Sub- and supercritical water treatment

Processing of lignin in sub and supercritical water can produce smaller fragments through breakage of the (ether) linkages and produce larger fragments trough cross linking between the reactive fragments, predominantly by Friedel-Craft mechanism [94–97]. Dealkylation and demethoxylation also occurs when processing lignin in a hydrothermal medium. The amounts of higher molecular weight residue can be minimized by simultaneous optimization of the reaction temperature, the residence time and the water density. In general, considering the low concentration of lignin which in turn causes low concentration of reactive fragments in water, the probability of the undesirable condensation reaction is significantly lower compared to the processes in which lignin is degraded in a dry form. On the other hand, due to the extremely high specific heat of water, the process heat of supercritical water process would be significantly high and the economic viability of the process is severely controlled by the extent to which the heat is recovered from the effluents.

The addition of alkali salts to subcritical water has been shown to have a positive effect on the oil production in subcritical water [98–101]. By increasing the reaction time, the yield of monomers reaches a maximum after which it declines due to severe repolymerization reactions. The yields of monomers are positively correlated with base concentration. However, regardless of the alkali and lignin concentration, the maximum yield of low-molecular weight products barely exceed one third of the initial lignin.

The addition of phenolics (e.g. phenol, p-cresol) [95,102,103] or other organics such as butanol [104] and boric acid [99] to the reaction mixture has proved to greatly facilitate the depolymerization of lignin in supercritical water, and more importantly, increase the product selectivity. Such improvement in the conversion and selectivity is achieved through the reaction of the phenol with the reactive fragments which consequently reduces the condensation reactions between the fragments. Therefore, one can expect that a large fraction of the depolymerization products have biphenyl dimer structures in which one phenolic moiety has originated from lignin and the second one from the co-solvent. The obtained products can be used as a high boiling solvent or it can be cracked into two aromatic molecules and partially recycle into the process.

5.4. Supercritical solvents

Isolated lignins can be depolymerized into soluble fragments in supercritical solvents at high yields. The most widely used solvents include ethanol [105–108] and methanol [109,110] but other organic solvents such as CO_2/acetone/water [111] and butanol [104] have been also used. The mixtures of alcohol and water, with substantially milder autogenous pressure, have been also found to be an effective medium for lignin depolymerization [108,112]. The depolymerization of lignin in organic solvents is typically conducted in the temperature range of 200–350 °C and high pressures. Lignin solvolysis processes can be categorized into two general groups: base-catalyzed depolymerization and hydrogenolysis. The hydrogenolysis processes in supercritical solvents for lignin depolymerization can be further divided into three subgroups: (i) fragmentation with pressurized H_2 gas, (ii) fragmentation with in situ hydrogen production from a hydrogen-donor solvent such as formic acid [113,114] which is thermally decomposed during the depolymerization reaction, and (iii) fragmentation with hydrogen produced from the partial reforming of the solvent in presence of a metal catalyst [110]. A near complete dissolution of technical lignins has been already reported in the literature. The molecular weight of the dissolved lignin ranges from about 150 to 2500, corresponding to a degree of polymerization of approximately 1–15. As this molecular weight distribution suggests, the dissolved lignin fragments has both liquid and solid fractions, the former of which has a molecular weight of approximately smaller than 300 and the latter of which contains all the trimers and larger oligomers. The individual yield of monomers can be up to few percent of the feed, but barely exceeds 5%. Furthermore, the boiling point of the

dissolved lignin fragments dramatically decreases upon hydrogenolysis to smaller molecules followed by hydrodeoxydation and hydrogenation which eventually leads to the formation of saturated hydrocarbons ranging from C_6 to C_{11}. This decrease in the boiling point of product allows for the separation and purification of the products at lower temperatures which in turn, would inhibit the undesirable repolymerization reactions that occur at higher temperatures. During hydrotreating of lignin, the percentage of the protons bound to aliphatic carbons increases while the percentages of protons bound to aromatic sites and oxygen decreases [110].

6. Gasification

Alike gasification of other biomass species, the decomposition products of lignin would ultimately be a mixture of small permanent gas molecules such as H_2, CO, CO_2, and CH_4 with varying ratios depending on the gasification temperature and pressure, presence of steam and oxygen, heating rate, and the feed elemental composition. However, as technical lignins often contain inorganics and sulfur incorporated into the structure during fractionation from biomass, lignin gasification products also include some ash and H_2S. The generation of combustible gases from lignin can be achieved by three distinct processes: (i) conventional gasification with oxygen and/or steam at high temperatures and a near atmospheric pressure, (ii) pyrolytic gas release in the absence of active agents (i.e. air, steam), and (iii) catalytic gasification in supercritical water which proceeds at moderate temperatures and high pressures.

The gasification products mixture, collectively known as syngas, already has proven industrial applications for the generation of electricity, pure hydrogen, and synthetic liquid fuels and chemicals. Furthermore, in contrast to pyrolysis, the product selectivity in gasification is inherently less problematic as the syngas composition can be easily adjusted through reformation, water–gas shift, selective oxidation, and methanation. Nonetheless, it should be realized that the primary products of gasification, at least on a pure basis, are significantly of lower value compared to the aromatics typically found in a pyrolysis bio-oil.

6.1. Conventional gasification

Due to its availability in large quantities, the literature on lignin gasification is mostly focused on conversion of black liquor, a by-product of papermaking process with rather high amounts of alkali lignin. Black liquor is an aqueous solution composed of lignin and hemicellulose residues as well as the inorganic chemicals used in the kraft pulping process. The major elements present in black liquor include carbon, oxygen, sodium, sulfur, hydrogen, and potassium. In conventional chemical pulping mills, the black liquor is fired in recovery boilers to recover the pulping chemicals and energy in form of steam and electricity. Gasification of black liquor for the production of syngas has been extensively studied over the past few decades, aiming at developing a more efficient technology for production of steam and electricity based on combined-cycle power generation as well as creating an opportunity to produce synthetic liquid biofuels in the mill. Partial combustion of black liquor in gasifiers holds many similarities to its conversion in recovery boilers (i.e. full combustion). In both processes, black liquor should be atomized first to allow for a better heat transfer to the droplets. In black liquor gasification, after the evaporation of the water content of the droplets, the organic content of the particles undergo pyrolysis and devolatization of gaseous compounds followed by partial combustion with under-stoichiometric amounts of oxygen. Finally the resulting char residue, which also contains significant amounts of inorganic salts in molten form, reacts with the surrounding gases (e.g. CO_2, H_2O) to gasify the remaining organic fraction and leave a particle that is (ideally) only composed of the inorganic matters to be regenerated for the pulping process. However, the behavior of black liquor which comprises of about 30% inorganics is considerably different from the relatively pure lignin obtained from black liquor precipitation. The composition of the syngas obtained from gasification of black liquor in a pilot plant facility in Sweden operated at 1000 °C and 28 bar was reported as 34.8% H_2, 28.5%CO, 33.6%CO_2, 1.4% CH_4 and 1.7% H_2S [115]. The synthetic gas can be used in gas turbine combined heat and power (CHP) systems or fed to a catalytic liquid fuel production process such as methanol synthesis [116]. Depending on the synthesis product, an intermediate gas separation step maybe required prior to the catalytic reactor to adjust the H2/CO/CO_2 ratios. The major challenges towards commercialization of black liquor gasification is corrosion at high temperatures caused by the presence of alkali compounds and the decrease in the S/Na ratio in the recovered chemicals which in turn increases the caustisizing demand.

6.2. Pyrolytic gas formation from lignin

Hydrogen and other combustible gases such as methane are released from lignin during pyrolysis at elevated temperatures. Decomposition of lignin by pyrolysis is rather difficult in contrary to cellulose and hemicellulose and it occurs over a fairly wide temperature range (e.g., 150–900 °C) and resulted in the formation of high solid residue (e.g. >40 wt%). A hydrogen yield of $\sim$21 mmol/g was obtained from alkali lignin by pyrolysis at 900 °C whereas only $\sim$5 mmol/g of hydrogen was produced from cellulose at the same operating conditions. The hydrogen yield from pyrolysis of lignin was negligible at temperatures below 450 °C after which it linearly increased with temperature for both organosolv and kraft lignin [117]. It was also shown that although hydrogen was continued to form at higher temperatures, the highest hydrogen generation rate was observed at temperatures around 600 °C [72]. A comparative study on fast pyrolysis of alkali and organosolv lignin revealed that organosolv lignin was more reactive in an inert atmosphere and resulted in higher gas yields compared to alkali lignin. However, the hydrogen mole fraction in the gas products of alkali lignin was higher than that of organosolv lignin [118]. The gas yield and hydrogen mole fraction increased by increasing the pyrolysis heating rate from 5 to 15 °C/min for both organosolv and kraft lignin [83]. Addition of H-ZSM5 and Co/Mo/Al_2O_3 catalysts significantly improved the hydrogen yields obtained from pyrolysis of lignin [73].

6.3. Supercritical water gasification

Catalytic supercritical water gasification (also known as hydrothermal gasification) is a promising technology for the production of hydrogen and methane from organic feedstock with high water contents as there is no need for drying prior to the gasification. A large body of literature exists on catalytic gasification of lignin and lignin-containing materials in supercritical water medium using solid nickel [119–123] and ruthenium catalysts [120,124–126]. It has been observed that regardless of the type of catalyst and the gasification temperature, lignin is substantially more resistant towards gasification in supercritical water medium compared to carbohydrates. Catalytic supercritical water gasification takes place at lower temperatures and higher pressures (e.g. 350–500 °C and 250 bar) compared to conventional gasification (e.g. 800 °C and 1 bar), which in turn favors high methane and low hydrogen yields at equilibrium. However, it is possible to obtain high hydrogen selectivity by preventing the methanation reactions through the design of

selective catalysts. The ideal catalyst for hydrogen production from lignin should exhibit the following attributes: high activity for opening the phenolic ring and the subsequent cleavage of C–C bonds, high activity for water–gas shift reaction and low activity for the cleavage of C–O bond while having a reasonable hydrothermal stability. Both nickel and ruthenium metals are generally active for hydrogenation of carbon dioxide and thus it is required to hinder their activity for the cleavage of C–O bond through addition of promoters [127,128] or changing the metal-support interaction and crystallite size [129]. It has been shown that the addition of alkali salts such as NaOH can somewhat increase the gas yields. Supercritical gasification of native lignin in lignin-containing feedstock such as wood and bark seemed to be easier compared to the isolated lignin from the kraft process [120] which contains higher percentage of refractory C–C interunit linkages [7]. Also, using both lignin and propyl phenol as a model compound of fragmented lignin, it has been found that water density only affects the initial lignin decomposition of lignin to lower molecular weight fragments [130].

7. End-use applications

Generally, the lignin-derived products can be used as fuels, solvents, chemical reagents, and polymers. Here, we briefly overview the potential applications of lignin-derived compounds as biorenewable fuels and aromatic chemicals. The polymeric applications of lignin (e.g. carbon fiber, polymer fillers, thermoset resins, adhesive, etc.) falls beyond the scope of this paper and one may refer to [8,131–133] for a review of such applications.

Fig. 10 depicts the primary thermochemical processes for the conversion of the isolated lignins and lignin-containing biomass. It also provides a time frame by which each of these technologies are likely to be implemented to produce a certain group of products. The implementation time frame is adapted from the report published by the Pacific Northwest National Laboratory in 2007 [8] and revisited based on the recent advances in the field and the authors' viewpoint. As shown in this figure, the lignin-based fuels fall into four categories: (i) solid lignin and lignin-derived chars (ii) liquid fuels obtained from selective depolymerization followed by catalytic hydrogenation and chemical modifications, (iii) hydrogen through gasification and water–gas–shift, and (iv) synthetic alcohols and Fischer–Tropsch liquid fuels from gasification syngas.

7.1. Fuels

The roadmap for the thermochemical conversion of lignin to liquid, gaseous and solid fuels is shown in Fig. 11. As discussed previously, there are two different directions for the conversion of lignin to combustible fuels: depolymerization and gasification. However, it is expected that higher yields, and hence a better process economy, can be achieved through the process integration. For example, the easier-to-depolymerize fraction of lignin can be processed to produce aromatics while the solid residue is sent to a gasifier to produce hydrogen required for fuel upgrading. The light hydrocarbons can be also catalytically reformed to yield syngas and hydrogen. Lignin and lignin derived compounds can be used as a fuel in the following forms: solid lignin and char, syngas, hydrogen and aromatics.

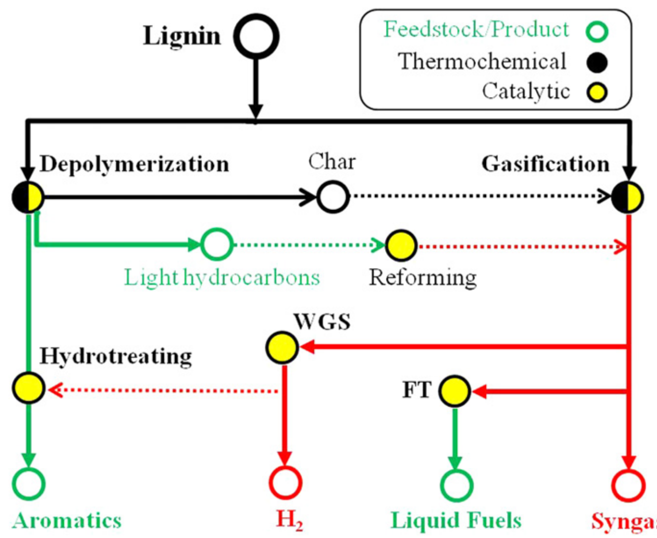


Fig. 11. Roadmap for the conversion of isolated lignin to liquid (green), gaseous (red) and solid (black) fuels. FT: Fischer–Tropsch synthesis, WGS: water–gas shift (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

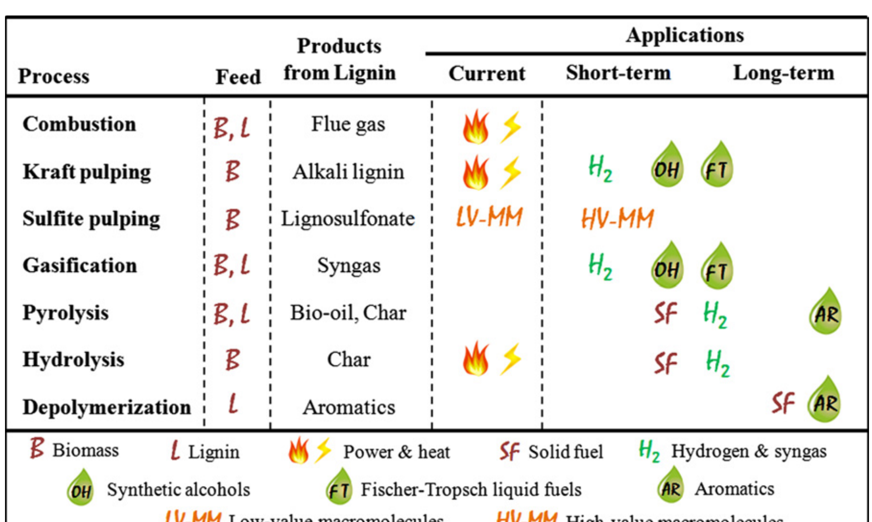


Fig. 10. Major processes, primary products and applications of isolated lignin and lignin-containing biomass. Production of hydrogen from the primary products involves gasification (or reforming) and water–gas shift reactions.

7.1.1. Solid lignin and char

Isolated lignins and the solid char produced as the byproduct of biomass hydrolysis can be combusted to generate heat and power which is thus far the most dominating use for the isolated lignins.

7.1.2. Syngas

Theoretically, gasification of one kilogram of isolated lignin with steam approximately yields 62 mol hydrogen and 53 mol carbon monoxide, corresponding to a H2/CO ratio of 1.2. However, this reaction is extremely endothermic and requires external heat to proceed. In the case of autothermal reforming, where the heat of reaction is provided by partial oxidation of the lignin, the yield of syngas would decrease to nearly 80% of the above numbers. The gas mixture obtained from lignin gasification can be used for the synthesis of methanol and Fischer–Tropsch fuels. The syngas can be combusted in gas turbines to generate heat and power.

7.1.3. Hydrogen

Pure hydrogen can be produced from further upgrading of the syngas through water–gas shift reaction followed by gas separation using pressure swing adsorption, resulting in about 80% increase in the overall hydrogen yield compared to raw syngas. The purified hydrogen can be used in several ways: as a clean energy carrier, for fuel upgrading in petroleum and biorefineries, ammonia synthesis, and in fuel cells.

7.1.4. Aromatics

As reviewed in Section 5, a variety of different processes can be employed to depolymerized lignin into its aromatic monomer constituents. Although none of these processes are able to achieve a high yield of monomers and high selectivity towards a certain compound simultaneously, even partial conversion and product separation of lignin monomers maybe economically viable. The boiling point and water solubility of lignin monomers and their derivates which are commonly found in depolymerization products versus their oxygen content are depicted in Fig. 12. The boiling point of the lignin-derived phenolics monomers reduces from 300–350 °C to below 100 °C through hydrodeoxygenation and hydrogenation. The total hydrogen demand for depolymerization and hydrodeoxygenation of lignin can be easily met by the reformation of the small molecules released during the process. For instance, production of one mole of *p*-cresol from its parent monomer in protolignin requires 4 mol of hydrogen; 2 mol for the release of monomer from lignin, 1 mol for cleavage of methoxyl group, and 1 mol for the hydrogenolysis of the propyl bond from the carbon at the α position. Steam reforming of the byproduct of these reactions (i.e. methanol and ethanol) generates a total of 9 mol of hydrogen. Given that aromatic hydrocarbons constitute about 35–50% and 26–30 of gasoline and diesel fuels [134], respectively, lignin depolymerization products can be readily blended into transportation fuels with little or no further processing.

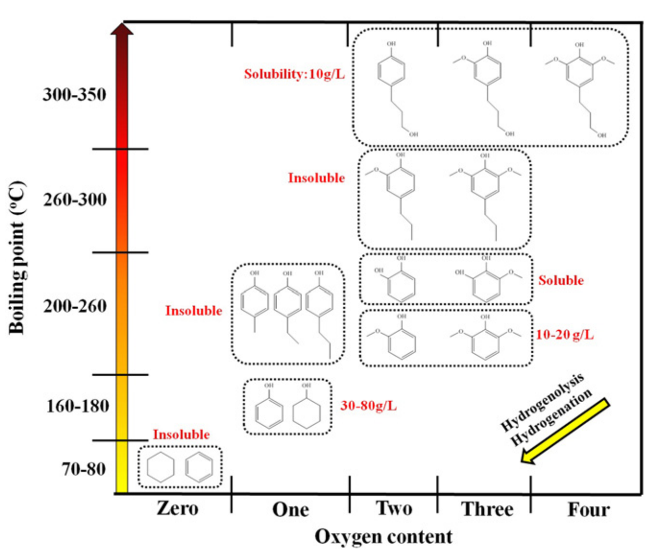


Fig. 12. Normal boiling points and water solubilities of selected hydrocarbons formed by hydrogenolysis, hydrogenation and dealkylation of lignin-derived monomers.

7.2. Aromatic chemicals

Low molecular weight aromatic compounds are commonly used in a variety of different industries as a solvent or chemical reagent. As demonstrated in Fig. 12, the phenolic monomers obtained from the depolymerization of lignin, either directly or with minor chemical modification, fall within this class of compounds. Concerning the use of the lignin-derived aromatics two distinct scenarios exist: (i) production of the most commonly used aromatics such as BTX (benzene, toluene, xylene) which are easy to incorporate into the existing industrial processes and products, and production of alkylated phenols with high degrees of similarity with the monolignols and attempt to modify the existing industrial processes and products to be able to cope these compounds. In both cases, product purification adds to the value of the lignin-derived molecules but impose additional energy and material loss. As a rule of thumb, the degree to which the use of mixed products, such as lignin depolymerization mixtures, can be tolerated decreases with the following order: fuels > solvent > chemical reagent. Therefore, the use of lignin depolymerization product mix; which is typically a complex mixture of molecules for the production of commodity and specialty chemicals needs to overcome more barriers than the technologies that aim to produce fuels and high-grade mix solvents from lignin. However, one should also take into the account the economic value of such products to give a more realistic evaluation of the opportunities. The application of lignin-derived compounds as a fuel has been already discussed in Section 7.1. The use of purified lignin-based compounds to replace the petroleum-derived aromatics in the existing industries is relatively straightforward and fall beyond the scope of this section as the challenging part will continue to be solely around the efficient conversion of lignin to such products with a desirable purity. Instead, here we overview how the aromatic lignin-derived solvents (LDS) cab be used as a biorenewable high boiling solvents (typically > 250 °C) at industrial scale, particularly in the context of future biorefineries.

The lignin-derived phenolic monomers, such as propyl guaiacol, can be implemented in biomass conversion processes in order to extract the biomass hydrolysis compounds from the aqueous acid solutions, to serve as the organic phase in the biphasic catalytic reactors in which carbohydrates are transformed into useful chemical platforms such as levulinic acid (Fig. 13), and to serve as a medium for the selective hydrogenation of these platform compounds to fuels and fuel blends such as gamma-valerolactone (GVL).

The alkyl phenols have shown to be effective solvents for the extraction of biomass-derived oxygenated compounds such as furfural, furfuryl alcohol, hydroxymethylfurfural (5-HMF), levulinic acid, and gamma-valerolactone from aqueous solutions containing mineral acids [57,135]. In addition to the high partition coefficient for the extraction of these molecules, the lignin-derived solvents do not extract the mineral acid which can be recycled back to the hydrolysis reactor, and they have a higher boiling point than these platform molecules which in turn dramatically decrease the energy consumption during the distillation stage required for product

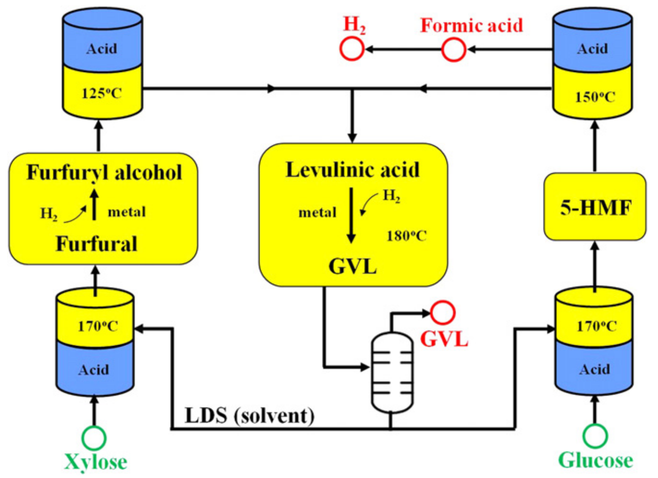


Fig. 13. Production of gamma-valerolactone (GVL) using solvents derived from lignin. Yellow: lignin-derived solvent (LDS), blue: acid aqueous phase (adapted from Ref. [67]) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

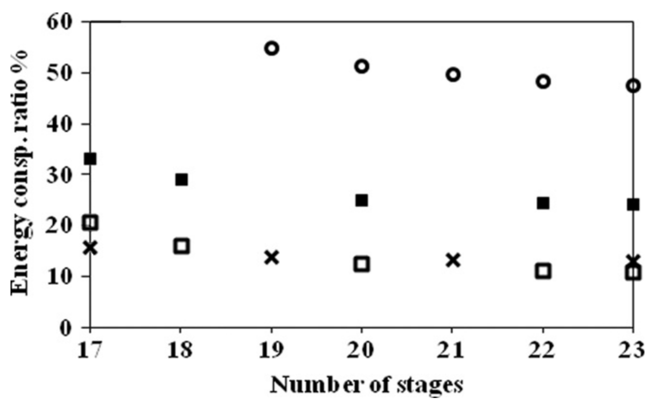


Fig. 14. Energy consumption ratio (defined as the ratio of the distillation energy consumption to the energy content of the recovered GVL) for separation of gamma-valerolactone (GVL) from the lignin-derived solvent (LDS) at different feed concentrations and entering temperatures vs number of distillation stages calculated using ASPEN PLUS. Feed: (○: 0.5 M, 20 °C), (■: 1 M, 20 °C), (□: 1 M, 200 °C), (×: 2 M, 20 °C).

separation. Fig. 14 shows the energy consumption for the separation of gamma-valerolactone produced from biphasic processing of xylose and glucose (Fig. 13) at different product concentrations and inlet temperatures. Furthermore, these alkylated phenols obtained from lignin are stable in the operating conditions typically utilized in biphasic reactors and the downstream hydrogenation steps. However, even if a fraction of solvent is hydrogenated to molecules with lower boiling points it would not have a detrimental impact on the combustion characteristics of the final products. In summary, the high-boiling alkylated phenols obtained from depolymerization of lignin seem to offer major technical and economical advantages if adapted to be utilized within the lignocellulosic biorefineries.

8. Outlook and policy recommendations

8.1. Summary and outlook

Lignin constitutes about a quarter of the lignocellulosic biomass, which has been identified as the most suitable type of biomass for the production of biorenewable fuels and chemicals. Lignin has higher energy content per unit mass than carbohydrates and it is the largest source of renewable aromatics on the earth. However, due to the complex structure and presence of various linkages between the monomers, the conversion of lignin to value-added compounds is substantially more difficult than that of carbohydrates. The thermal and oxidative instability of the lignin fragments make lignin processing even more challenging. In the future, lignin will be processed not only in the pulp industry but also in biorefineries designed to maximize the value extracted from the lignocellulosic biomass. Kraft process is currently the dominating method for the production of chemical pulps and it is expected to retain its share in the future. Therefore, a significant portion of the available isolated lignin will remain to be the kraft lignin, which is relatively more difficult to process due to its sulfur content and higher percentage of the refractory C–C bonds. Since pulp and paper industry is a capital-intensive industry, it is unlikely that a dramatic change in the pulping processes occurs in the near future. Therefore, developing technologies that can be readily integrated in the current pulp mills is the most desireable approach. For instance, the implementation of a gasifier to currently operational kraft mills that are limited by the capacity of the recovery boiler will bring considerable benefits to the mill by increasing the both pulp production capacity and energy recovery from the spent liquor simultaneously. In contrast to pulp and paper industry, biorefineries can be designed in such way that they take the most advantage out of each fraction of biomass. In this context, lignin would not be entirely regarded as a low grade solid fuel but it can be at least partially converted to value-added compounds. There are two different thermochemical approaches for the valorization of lignins: gasification for generating syngas followed by the subsequent conversion of syngas to Fischer–Tropsch synthetic fuels, synthetic alcohols, and hydrogen; and depolymerization to yield aromatics and hydrocarbons with a molecular weights ranging from about 100 to 300 Da.

Within the context of lignin processing, gasification can be considered both as a standalone process for converting lignin into syngas or as an economizer which use the harder-to-process fraction of the lignin from an adjacent depolymerization process. The main advantages of gasification include feed flexibility and high product selectivity, allowing for ease of integration within pulp mills and biorefineries alike. Another advantage of gasification is its potential for the carbon capture if using oxygen instead of air, which in turn, will reduce the overall emissions of the mill and will have positive impact on carbon credits. However, conventional gasification is conducted at severe operating conditions and it still requires further development before it is fully commercialized.

Depolymerization is another approach for the production of fuels and chemicals from lignin. Compared to gasification, the depolymerization processes are typically conducted at milder operating conditions, and the monomeric products have a higher economic value compared to syngas because the aromatic products can be readily blended into current transportation fuels or used in chemical industry. However, the depolymerization processes usually result in low conversions, a wide range of monomeric compounds, and large amounts of oligomeric residues while consuming hydrogen for upgrading and stabilizing the product mixture. The byproducts of lignin depolymerization, namely char and light hydrocarbons such as methanol, should be utilized to improve the process viability. For instance, in a hypothetical case, lignin can be depolymerized to produce 20–40% of monomeric compounds while the oligomeric solid residue is fed into a gasifier, and the light carbohydrates are catalytically reformed, allowing for syngas generation from both byproducts. Another opportunity for pulp mills and biorefineries may arise from coupling of the organosolv or biphasic delignification, for example

by ethanol or phenol, with a downstream catalytic hydrogenolysis process in the organic solvent to obtain high value phenolic monomers. In addition to the coproduction of hydrogen (or syngas) which can serve as the tie component between the depolymerization and gasification processes, the aromatic products of lignin depolymerization can be used in biphasic biomass conversion reactors in biorefineries to allow for processing of higher feed concentrations while resulting in a high selectivity compared to the conventional single phase reactors. An example of such would be the use of the lignin-derived alkylated phenol solvents for the conversion of C_6 and C_5 carbohydrates to levulinic acid in multiple biphasic reactors through an intermediate formation of 5-HMF and furfural, respectively.

Several factors will collectively demand and motivate researchers and industry for developing more advanced lignin conversion processes in the future.

1- The decline in the supply of conventional fossil resources which are currently the main source of transportation fuels and aromatics.
2- The higher oil prices in the future, caused by the reduction in the supply capacity and the increase in the demand.
3- The ever-tightening environmental regulation will require a smart and efficient use of all fractions of biomass, including lignin, in order to reduce the overall emissions and achieve more sustainable economics.
4- The growth in lignin production capacity due to the development of lignocellulosic biorefineries. Also, as the pulping processes become more energy-efficient, they require smaller amounts of a "low-grade" fuel such as black liquor to supply the process heat, resulting in further increase in the amount of available lignins.

The efficient use of lignin has both direct and indirect benefits with regard to reducing the greenhouse gas emissions. It can directly produce biorenewable fuels and chemicals with a low carbon footprint while imposing a minimal impact on food. Additionally, the conversion of lignin to the value-added products will improve the viability of the lignocellulosic biorefineries. Consequently, even partial conversion of lignin can potentially make a large impact by enabling the conversion of the easier-to-convert fraction of biomass (i.e. carbohydrates) to biofuels.

8.2. Policy recommendations

As set out in the Introduction section of this paper, the increasing global population and the desire to increase the calorific value of the daily food portion per human will increase the amount of biomass produced. This hampers the potential for farming of dedicated energy crops as the land mass is restricted, but simultaneously will increase the amount of agricultural byproducts generated. These byproducts are mainly lignocellulosic and are often not utilized but seen as waste. Consequently, if food and bioenergy supply shall be increased, it is of paramount importance to utilize this lignocellulosic biomass. Utilizing these byproducts is of huge environmental benefit as it optimizes the economics and the environmental burden of farming and processing. Herein, we establish two main pathways for the utilization of the product/byproduct lignocellulose: (i) conversion to hydrogen or synthesis gas and (ii) conversion to value-added materials. Both routes are viable and policies and incentives should ideally support research, development, and commercialization for both of these routes.

Currently, the pulp and paper industry is the largest existing lignocellulosic-based industry. However, given the relatively slow pace of this industry in adopting the emerging biorefinery concepts, new regulations are required to regulate slow movers and incentivized implementation of the above technologies. A balanced approach that includes mandates and regulations is likely the ideal approach. These command-and-control policy levers can ensure the efficient use of lignin and have the additional benefit of reducing the environmental impact and renewal of the forest product industry while bottom-up, incentive-based policies like subsidies and R&D incentives can be used to accelerate growth and investments in integrated biorefineries that efficiently use biomass holistically.

Policy makers have to set framework and promote lignin conversion in order to make the dual goal mentioned achievable. Combining command-and-control policies that regulate offenders with incentive-based policies that support upcoming green businesses will be critical for efficient use of biomass and moreover, for achieving the dual goal of providing sufficient food and bioenergy.

Herein, we have set out routes to efficient lignin utilization and the crucial points that have to be improved in order to achieve the above-mentioned dual goal. The analysis provided within the review provides policy makers with a clear roadmap and lays the fundament for targeted policy making.

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